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PAPER

Early damage detection of epoxy via poly(vinyl cinnamate) mechanophore using Fourier transform infrared spectroscopy

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Abstract

The employment of mechanophores and mechanochemistry in materials has enabled the development of novel force-responsive materials. Studies exploring the force sensing capabilities of the UV-dimerized cinnamoyl moiety have shown that after severing its cyclobutane bond under an external force, the moiety will revert back to its initial fluorescent state. Current fluorescent detection methods, however, fail to properly detect cyclobutane mechanophore activation in highly opaque samples. In this study, we apply Fourier transform infrared spectroscopy technique to measure a composite's chemical structure and examine activation of the cinnamoyl moiety's cyclobutane bond, regardless of sample transparency. Samples containing 10 wt% poly(vinyl cinnamate) as the active mechanophore, as well as set of samples with an additional 0.5 wt% carbon nanotubes, used to create a completely opaque composite, were developed. Both composites showed an increase in peaks at 1650 cm^{-1} and 1635 cm^{-1} after strain, which correspond to the *cis* and *trans* isomers of the fluorescent double-bond in the cinnamoyl group. A statistical difference in peak height occurs as early as 4% strain—before the yield point of the composites—indicating that early signal detection is possible. This improved sensing method provides a simpler, faster method for early signal detection over fluorescent imaging.

1. Introduction

Mechanophores are force-responsive moieties which undergo a chemical reaction or response to an external applied tensile or compressive force. They have been incorporated in thermoplastics, crosslinked polymers, and block copolymers and used to study the mechanical responsiveness under stress at the molecular level by detecting chain breakage within these polymer networks [1–8]. Studies have shown that mechanophores can be incorporated in the backbone of linear polymers to provide signal detection in the presence of mechanical force [9–11]. For example, a study examined the process in which colorless spiropyran undergoes a ring-opening reaction when applied with a tensile force to form a red-colored merocyanine [8]. However, this color-change as a form of signal for damage detection was not generated until after significant and permanent mechanical damage had been applied. Instead, focusing more on the ability to detect damage or potential failure as early as possible would allow for great progress in material and mechanical characterization fields.

Two moieties in particular, cinnamoyl and anthracene, can dimerize using ultraviolet light to form a force-sensitive and highly strained bond that can be severed by the external application of a mechanical force [12–14]. When severed, these bonds become fluorescent with an emission at 500–550 nm and 365–415 nm respectively. This fluorescence enables the ability to g within the material. It is also suggested that the fluorescent response intensity within the region of 6%–15% strain seems to be linear with respect to the applied strain on the sample [14, 15]. Previous work has incorporated cinnamoyl groups into an epoxy thermoset by mixing 1,1,1-tris(cinnamoyloxymethyl) ethane (TCE) [14]. In addition, the anthracene moiety has been applied using dimerized anthracene carboxylic acid (DiAC) as a mechanophore particle distributed throughout an epoxy matrix [15]. These samples each underwent compressive forces with varying strains and mechanophore loadings to examine the signal generation abilities of the embedded mechanophore. DiAC samples were capable of generating

stress-response signal as early as 4% strain, while TCE samples generated signals at approximately 6% strain [14, 15]. Poly(vinyl cinnamate) (PVCi) is a vinyl polymer—each monomeric unit containing a cinnamoyl moiety—that can be UV irradiated to create a cross-linked matrix [16]. PVCi can be mixed with standard epoxy and then irradiated to readily form force-sensitive cyclobutane bonds as a cross-linker for PVCi.

Although the development is promising, there are several limitations using fluorescence as a detection method. First, samples must be transparent in order to properly examine for fluorescence. Composites utilizing carbon-based reinforcement methods such as carbon nanotubes (CNTs), carbon nanofibers (CNFs) and carbon black are opaque and therefore are incapable of generating a sufficient signal using current fluorescent detection methods. In addition, fluorescent signal generated from opaque samples show only the mechanophore activation at the surface of the material. This signal may not be strong enough to accurately characterize mechanophore response using fluorescence microscopy. Here, we propose that signals of samples incorporated with mechanophores can be detected using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). ATR-FTIR is advantageous over standard transmittance FTIR because it allows for surface characterization of materials and is capable of measuring samples with higher density and little to no transparency [17, 18]. Signal generation from molecular scission of strained bonds can be compared to a reference peak in order to normalize the data, and this ratio could be used to characterize and detect damage of the dimerized cinnamoyl and anthracene moiety samples without the need for fluorescence. In addition, ATR-FTIR may also improve upon current detection capabilities of only 6% strain for cinnamoyl based mechanophores.

With employment of ATR-FTIR, mechanophore signal detection capabilities could allow for increased sensitivity and detection at earlier strains. In this study, the cyclobutane bonds are embedded within the epoxy matrix in order to generate a signal before the yield strain of the bulk epoxy composite. This form of precursor detection occurs with the elastic region of the composite and before any early stage mechanical deformation. Therefore, it is important to note that the damage observed in this study is not the damage occurring to the bulk matrix, but rather the damage occurring to just the cyclobutane bonds present within the crosslinked PVCi cinnamoyl groups.

2. Methods

2.1. Preparation of mechanophore-embedded epoxy matrix composites

Mechanophore embedded epoxy samples were prepared by first dissolving 0.6 g of poly(vinyl cinnamate) (average M_n 40 000, Sigma Aldrich) and 4.25 g of epoxy resin (diglycidyl ether of bisphenol F, military grade, FS-A23) with 5 ml of dichloromethane (99.8%, Sigma Aldrich). For completely black samples, multi-walled carbon nanotubes (>90%, industrial grade, OD: 10–30 nm, US Research Nanomaterials, Inc.) were added during this step with a loading of 0.5 wt%. The solution was then sonicated at 21% amplitude for 20 s to ensure that the sample was completely dissolved and adequately dispersed. The dichloromethane was then removed through rotary evaporation at 40 °C for 30 min. Next, 1.15 g of hardener (diethylenetriamine, military grade, FS-B412) was added after rotary evaporation to make 6 g total of sample. The sample was then impeller mixed for 5–10 min at 200 rpms to ensure that the hardener was evenly mixed with the resin and poly(vinyl cinnamate) (PVCi). Immediately after mixing, the sample was poured into 8 × 3 × 4 mm rectangular molds, irradiated for 4 h with a 302 nm UV lamp, and left overnight to cure at room temperature.

2.2. Characterization

In order to activate the embedded mechanophore in the epoxy network, ample strain would need to be applied. For this reason, the samples were compressed to varying strains in order to test at what strain the mechanophore activation would be seen on the FTIR. Molecular scission of the cyclobutane formed after UV irradiation can be monitored. After applying mechanical force, the intensity of the wavenumber associated with the conjugated double bond in PVCi is hypothesized to increase. By examining the relatively intensity of this bond with respect to applied bulk strain, signal detection should be capable. Assuming PVCi is evenly dispersed throughout the epoxy and is at high enough loading, there should be enough cyclobutane bonds at the surface of the material to generate ample signal. A Test Resources 800L Compression Test System was used to test samples at 2%, 4%, 6%, and 15% strain at strain rate of 1 mm min⁻¹. ATR-FTIR spectra were taken with a Bruker IFS 66V/S FTIR, wide-band Mercury Cadmium Telluride (MCT) detector, KBr mid-IR beamsplitter, and a Pike diamond-ATR module from 4000 cm⁻¹ to 400 cm⁻¹.

3. Results and discussion

3.1. Development and validation of ATR-FTIR detection methods

Development and validation of a new ATR-FTIR detection method was necessary before evaluating a full range of mechanophore loading and varied strain experiments. Due to the nature of FTIR spectra, weight loading of poly(vinyl cinnamate) (PVCi) embedded into the epoxy network as well as morphology of the sample surface both

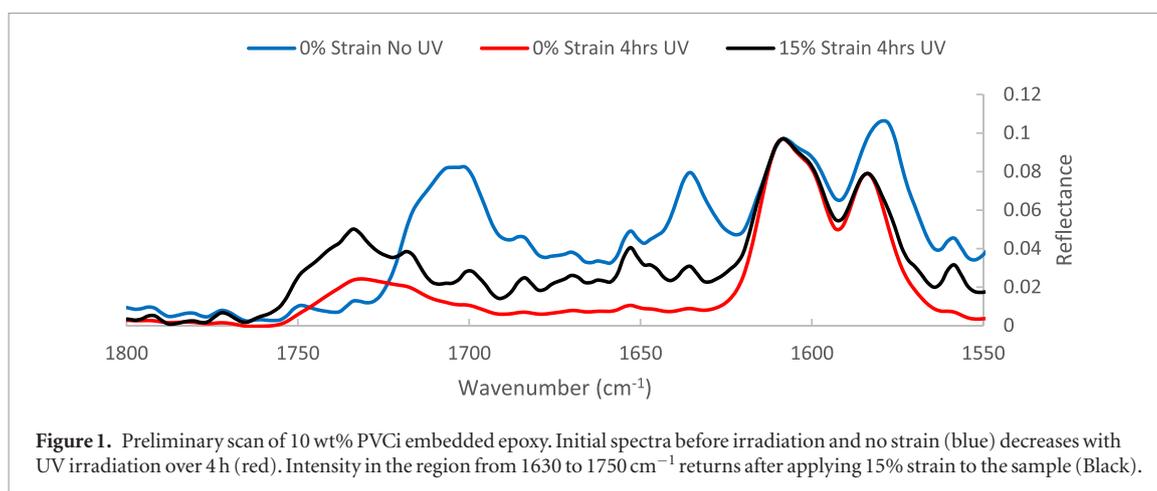


Figure 1. Preliminary scan of 10 wt% PVCi embedded epoxy. Initial spectra before irradiation and no strain (blue) decreases with UV irradiation over 4 h (red). Intensity in the region from 1630 to 1750 cm^{-1} returns after applying 15% strain to the sample (Black).

are important factors in determining the viability of early damage detection. When measuring spectra of a solid sample, it was important that the sample surface maintains as much contact with the ATR diamond as possible to ensure a strong signal. However, due to the nature of the sample surface—especially at high strains—signal strength varied due to surface deformation and crack formation. To counteract this, a neutral reference peak was chosen at approximately 1575 cm^{-1} , corresponding to an aromatic carbon–carbon double bond, to normalize each spectra and provide a direct comparison. For preliminary data, a small batch of epoxy with 10 wt% PVCi loading was made to ensure a proper signal strength in the FTIR. Spectra were taken with no UV irradiation at 0% strain, 4 h UV irradiation at 0% strain, and 4 h UV irradiation at 15% strain. Figure 1 shows the results obtained from these spectra. Samples with no UV irradiation and no strain show an evident peak at approximately 1635 cm^{-1} , corresponding to the UV active carbon–carbon double bond in PVCi. Peaks are also present at approximately 1710 cm^{-1} , corresponding to the carbon–oxygen double bond in PVCi. After irradiation, the carbon–carbon double bond peak at 1635 cm^{-1} disappears, and the carbon–oxygen double bond peak at 1710 cm^{-1} shifts to 1732 cm^{-1} due to the change in conjugation [13]. After 15% strain, the UV active carbon–carbon double bond recovers approximately 28% expression from its initial peak, indicating the breaking of these bonds due to mechanical strain. It is important to note that the entire region between approximately 1730 and 1620 cm^{-1} had a significantly higher reflectance before irradiation and after compression. This overall increase in reflectance could be used as an indication of signal detection. However, the peak at 1635 cm^{-1} was selected as the point of analysis due to its correspondence to the mechanochemistry involved in the cinnamoyl moiety.

Control samples of neat epoxy with no mechanophores were run under 0% and 15% strain to ensure that a change in spectra at 1635 and 1710 cm^{-1} were not intrinsic to mechanical force applied to the epoxy network. Figure 2(a) shows the normalized results obtained for these spectra. Assuredly, all samples showed change within standard deviation for before and after compression, indicating there was no change due to mechanical force.

3.2. PVCi mechanophore without CNTs

Much like our preliminary experiment, epoxy samples containing 10 wt% PVCi were prepared without any loading of CNTs. Because these samples did not contain CNTs, they were translucent and therefore comparable to previous work using transparent samples with fluorescent imaging. Before the samples were compressed, a spectra was taken of each sample designated for each compression in order to provide a baseline and develop a distribution of the natural deviation between samples. Once compressed to their designated strain, a spectra was then taken immediately after of the same sample and compared to the corresponding unstrained spectra. Two spectra were taken per sample, with two samples per strain. Between two batches, a total of eight replicates per data point were taken to provide a definitive distribution. Figure 2(b) shows an overlay of scans from one batch. Lower strains tend to show a lower relative peak height compared to those of higher strain, with the general trend of increasing peak height with increasing strain.

The ratio of peak intensity of 1575 cm^{-1} (aromatic reference peak) to 1635 cm^{-1} (trans-isomer of photoactive double-bond) was taken to show the change with increasing strain as well as the standard deviation for each data point. Figure 3 shows a plot of this data. As evident from this graph, there is a clear decreasing trend with respect to the ratio of 1575 cm^{-1} to 1635 cm^{-1} , with statistical difference occurring at 4% strain. Since the 1575 cm^{-1} peak is considered a constant peak as proven by our neat epoxy control sample, the decrease in peak ratio indicates that the peak at 1635 cm^{-1} is increasing. This is significant when compared to previous literature using cinnamoyl moieties [14]. Being capable of sensing at 4% is an improvement over previous TCE results, which were only capable of sensing at 6% strain, just after the yield point of the epoxy sample. However, after 4% strain all higher strains were not statistically different from each other. This may suggest that the mechanophore activation for this sample does not

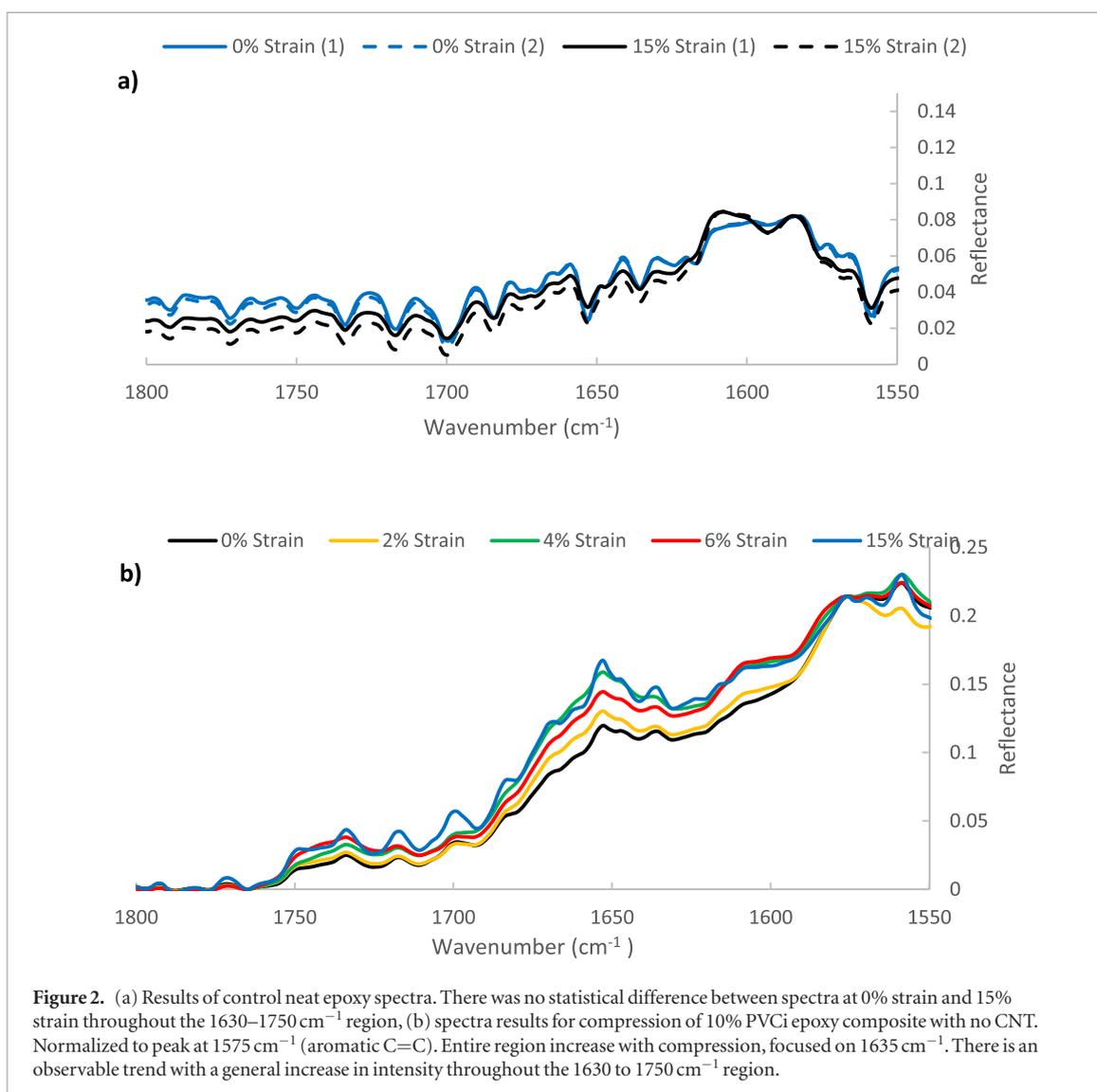


Figure 2. (a) Results of control neat epoxy spectra. There was no statistical difference between spectra at 0% strain and 15% strain throughout the 1630–1750 cm^{-1} region, (b) spectra results for compression of 10% PVCi epoxy composite with no CNT. Normalized to peak at 1575 cm^{-1} (aromatic C=C). Entire region increase with compression, focused on 1635 cm^{-1} . There is an observable trend with a general increase in intensity throughout the 1630 to 1750 cm^{-1} region.

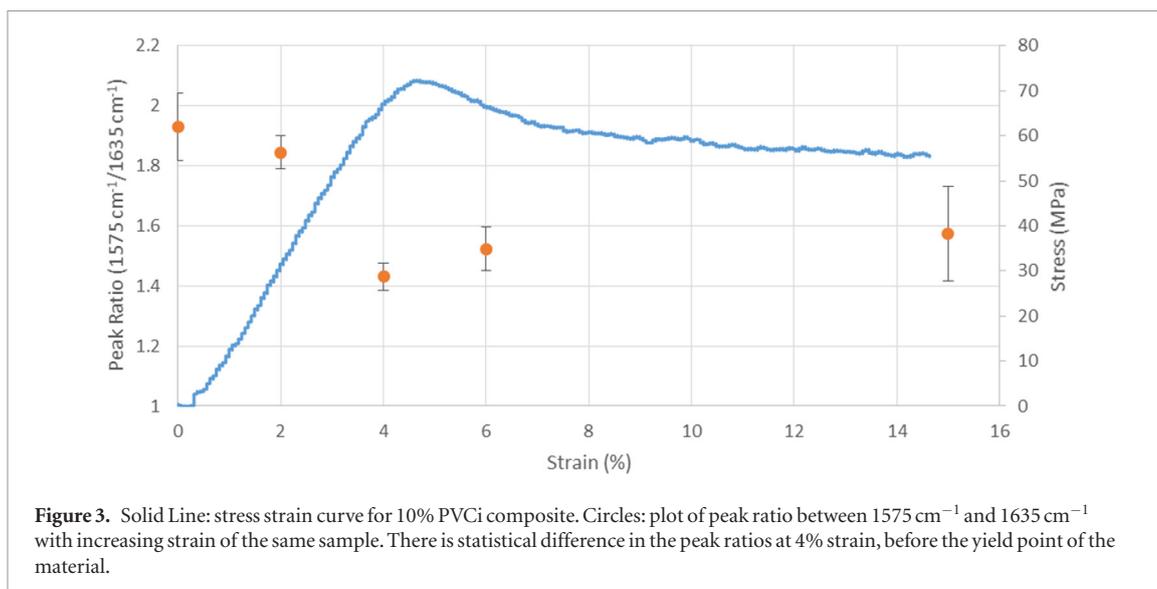
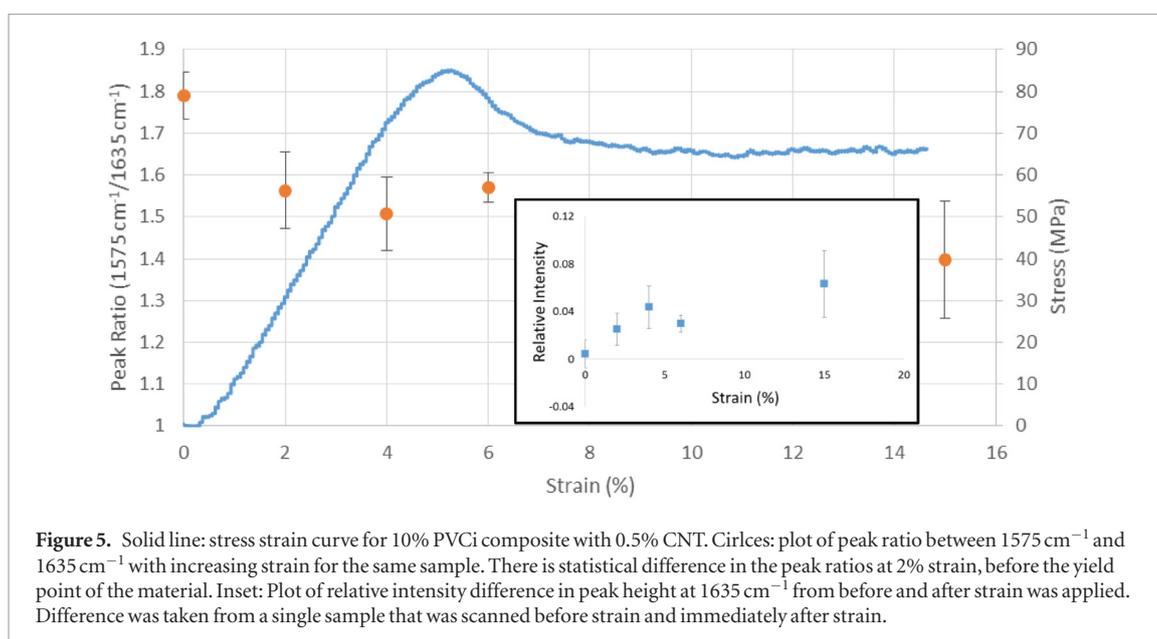
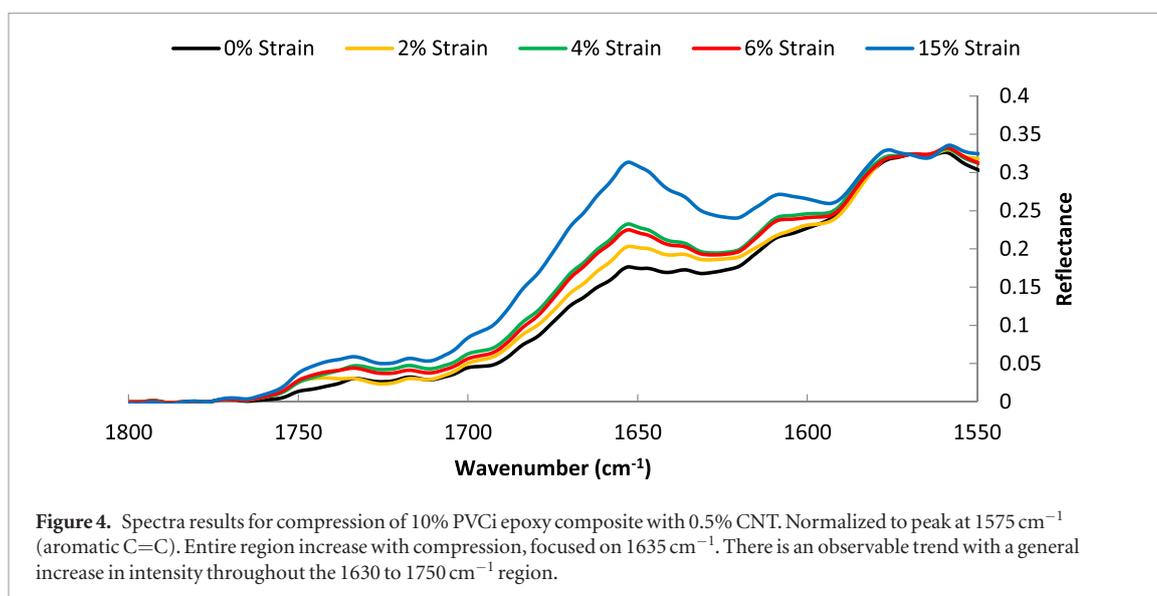


Figure 3. Solid Line: stress strain curve for 10% PVCi composite. Circles: plot of peak ratio between 1575 cm^{-1} and 1635 cm^{-1} with increasing strain of the same sample. There is statistical difference in the peak ratios at 4% strain, before the yield point of the material.

increase with increasing strain, like previous literature suggests [13, 14]. Instead, it suggests that a simpler, binary activation occurs for the embedded network at a certain load. Due to the small detection surface that the FTIR examines, it can be hypothesized that once enough force is applied to the examined surface, the mechanophores in this region are fully activated and displays a binary response. Previous work utilized fluorescence imaging, which examines the entire sample surface. Since the force applied at an individual point in the surface of the material



varies, mechanophore activation will vary slightly across the entire surface. As the net force applied across the material increases, this ‘average’ activation increases linearly with respect to the overall force.

3.3. PVCi mechanophore epoxy with CNTs

Similar to the standard 10 wt% PVCi epoxy samples that were previously discussed, additional samples were made with 0.5 wt% CNT. CNTs are commonly used to improve mechanical properties by reinforcing the thermoset [19–22]. However, for the purpose of this experiment they are simply used to create a completely opaque sample using a common structural additive. Since these samples cannot be measured using standard UV fluorescent imaging, ATR-FTIR spectra was employed to utilize the peak height at 1635 cm^{-1} in order to detect signal before the yield point of the sample. Similarly to the previous samples, two spectra were taken for each strain. Spectra were taken before and after strain for each sample. Figure 4 shows a plot of this spectra taken. Much like the standard 10 wt% PVCi samples, a clear trend with increasing peak height at 1635 cm^{-1} is observed with respect to increasing strain. Figure 5 shows a plot of this data with respect to the stress-strain curve, while its inset shows the difference in peak height between the strained sample and the initial unstrained scan of the same sample.

A second scan of the initial unstrained sample was taken to observe any natural deviations in peak height. By comparing the compressed samples to their uncompressed counterparts, there is clear statistical difference once again at 4% strain. These results reinforce the previous work with standard 10 wt% PVCi samples, and are a significant improvement over previous work with DiAC and TCE. Firstly, the sensing of an opaque, black sample was successfully achieved using ATR-FTIR. Previous work with UV-fluorescence imaging was incapable of measuring

a sample with either property. Secondly, the previous particulate mechanophores sensed at just before the yield point of the epoxy material at approximately 6% strain. Sensing before 6% strain has not previously been reported using cinnamate groups as active mechanophores within an epoxy thermoset. However, there is more work to be done regarding sensing with ATR-FTIR.

4. Conclusion

The employment of mechanophores and mechanochemistry in materials has allowed for many novel, force-responsive materials to be developed. Previous work has shown that samples embedded with cinnamoyl-based mechanophores are capable of UV-fluorescence after being applied a mechanical force. ATR-FTIR offers the ability to measure the material's chemical make-up at the surface and examine the activation of the cyclobutane bond within the cinnamoyl group of the mechanophore, regardless of sample transparency. Samples were prepared with 10% by weight PVCi as the active mechanophore in an epoxy thermoset, as well as samples with an additional 0.5% by weight CNT to create a completely opaque composite. Both samples were capable of sensing at 4% strain, which is an improvement over the previous work's ability to sense at 6% strain using UV-fluorescent imaging. Overall, FTIR analysis provides a simpler, faster, and more sensitive method for detecting cyclobutane mechanophore damage with a wider availability over current fluorescence detection methods.

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